

STUDY OF THE 10 MICRON CONTINUUM OF WATER VAPOR

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16. Abstract  Radiation attenuation by atmospheric water vapor is considered in this work. A formula based on laboratory data is recommended for approximating continuous absorption in the spectral region in question. Data of various authors and of full-scale measurements and laboratory experiments are compared. The authors conclude that only molecular absorption need be taken into account under clear atmospheric conditions during the warm part of the year, while in winter or in cloudy conditions, the effect of aerosol can be significant.			
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## STUDY OF THE 10 MICRON CONTINUUM OF WATER VAPOR

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### Introduction

Improving the methods of thermal sounding of the atmosphere /4\*  
from artificial earth satellites requires deeper knowledge of the patterns of radiation propagation through the 8-13  $\mu$  window of relative transparency of the atmosphere. The attenuation of radiation in this window is determined by the following main factors: continuous (uninterrupted) radiation attenuation by atmospheric water vapor; aerosol absorption and scattering; selective absorption by weak lines of small components of the atmosphere. The effect of the latter factor is relatively slight in narrow sections of the 8-13  $\mu$  window which are free of absorption lines. The effects and the roles of the two other factors are the subject of this discussion.

This work presents the results of laboratory studies of radiation attenuation by the water vapor continuum for 10.6  $\mu$  radiation under different conditions and a comparison of these results to the data of full-scale measurements.

### Measurement Procedure and Instrumentation

Experiments to study 10.6  $\mu$  attenuation were conducted in a multichannel optic cell of the White type with a base of 50 m,

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\*Numbers in the margin indicate pagination in the foreign text.

which was equipped with the appropriate measurement apparatus and which makes it possible to investigate gas layers several kilometers thick [1]. A CO<sub>2</sub> laser of the LG-22 type was used in the measurements; the laser radiation spectrum was monitored constantly by means of a spectrometer with a diffraction grating of 100 lines per millimeter. The transmission of radiation of an LG-126 laser with a wavelength  $\lambda=0.63 \mu$  was measured for evaluation of the role of water aerosol. /5

Laser radiation modulated with a frequency of 100 Hz was received alternately before and after passage through the cell by the same photoreceiver (a photoresistor based on germanium alloyed with gold, cooled with liquid nitrogen) and, after amplification and rectification, was recorded on charting tape of a V-014 self-recording device with a time constant of 0.25 s. The level of radiation transmission was determined from the ratio

$$T = \frac{I / I_k}{I^0 / I_k^0}$$

where  $I$  is the intensity of radiation which has passed through a cell filled with the gas under investigation;

$I^0$  is the intensity of radiation which has passed through a vessel evacuated to a residual pressure of  $10^{-4}$  tor;  
 $I_k$  and  $I_k^0$  are the radiation intensities before entry into a gas-filled cell and an evacuated cell, respectively.

Water vapor was fed in small portions from a vaporizer into the preliminarily evacuated (to  $10^{-4}$  tor) cell; the water vapor concentration was determined according to the pressure, measured with a mercury manometer. Nitrogen evaporated from Dewar vessels was then added to the cell in experiments with an expanding gas. The water vapor concentration in the mixture of N<sub>2</sub>+H<sub>2</sub>O was additionally monitored in regard to the change in the weight of a portion of phosphoric anhydride P<sub>2</sub>O<sub>5</sub> after a gas sample of a definite volume had been pumped through it. The gas in question

was kept in the cell at the required temperature (for minutes in pure water vapor and for hours with mixtures of  $N_2+H_2O$ ) until an equilibrium state emerged, monitored according to the stability of the intensity of the beam passing through the vessel.

The total random error did not exceed 8% in experiments with pure water vapor and 10% in experiments with vapor mixtures with nitrogen or air for any individual measurement of the radiation transmission T. /6

### Measurement Results

Measurements of the  $10.6 \mu$  radiation transmission by pure water vapor and its mixtures with nitrogen were conducted at various temperatures in the range  $\theta=284-353^\circ K$  in layers with  $L=1.99$  and  $2.98$  km. The overall concentration of water vapor reached a level  $w=5-6$  cm of a deposited layer of water, which conforms to the maximum value of  $w$  in a vertical column of the terrestrial atmosphere. The total pressure of the mixture of  $N_2+H_2O$  amounted to 1 atmosphere in experiments with an expanding gas.

Fig. 1 presents the results of measurements of the radiation transmission by pure water vapor and a mixture of water vapor with nitrogen at  $\theta=290^\circ K$  and  $L=2.98$  km. Fig. shows that the nitrogen pressure ( $P_{N_2} \approx 1000$  mbar) only slightly affects the level of  $10.6 \mu$  radiation absorption by water vapor throughout the humidity range examined.

Fig. 2 presents the results of measurements of  $10.6 \mu$  radiation transmission by pure water vapor at temperatures of 353, 323, 293 and  $284.5^\circ K$ . With a temperature increase by approximately 25% at a constant humidity level, the optic density  $\tau = -\ln T$  decreases to approximately one third of its previous value, i.e., a so-called negative temperature dependence is observed.

The solid curves in figs. 1 and 2 were calculated by the following approximation formula,

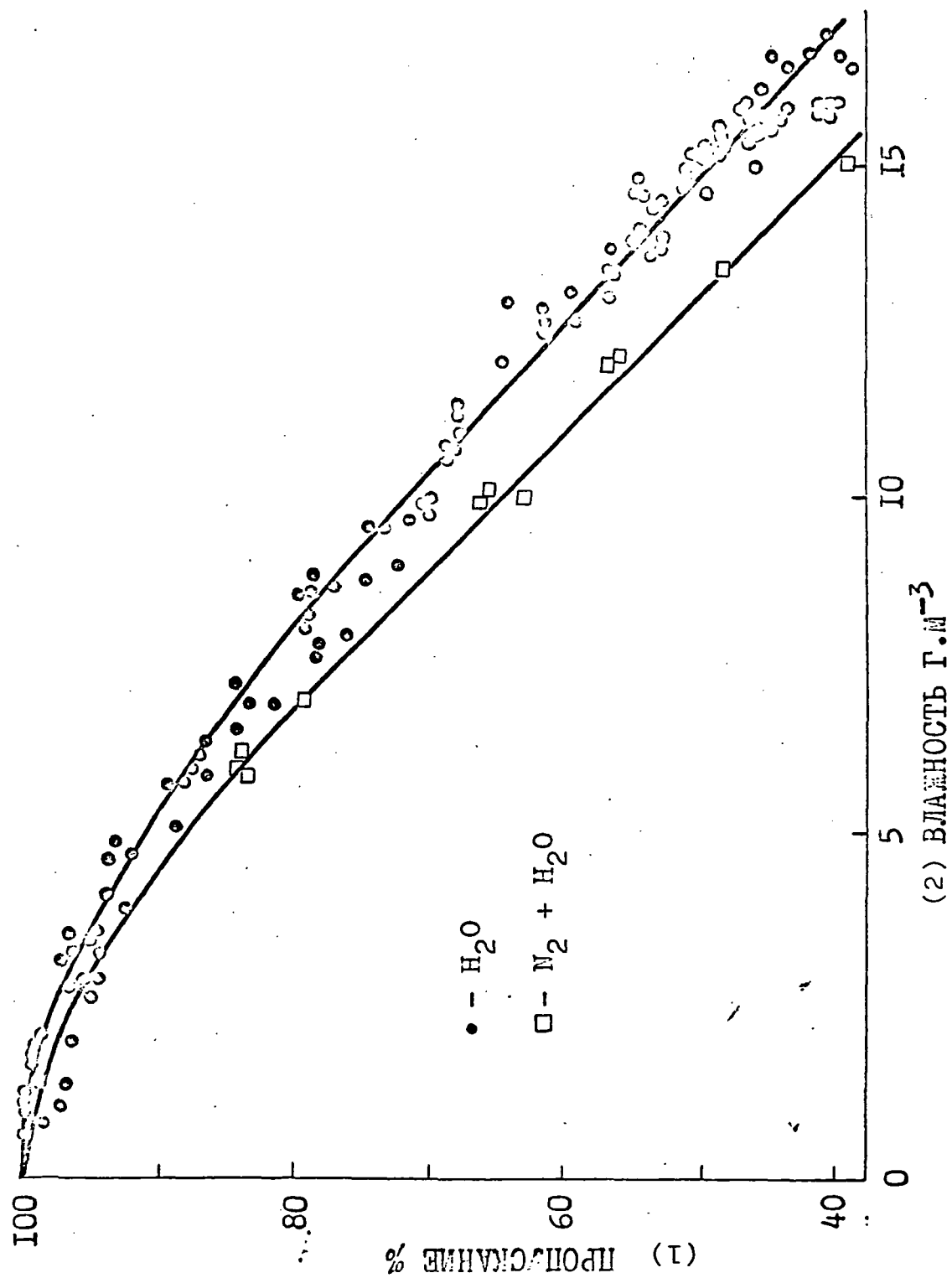


Fig. 1. Transmission of  $10.6 \mu$  radiation by water vapor.  
 Key: (1) transmission, in %; (2) humidity, in  $g/m^3$ .

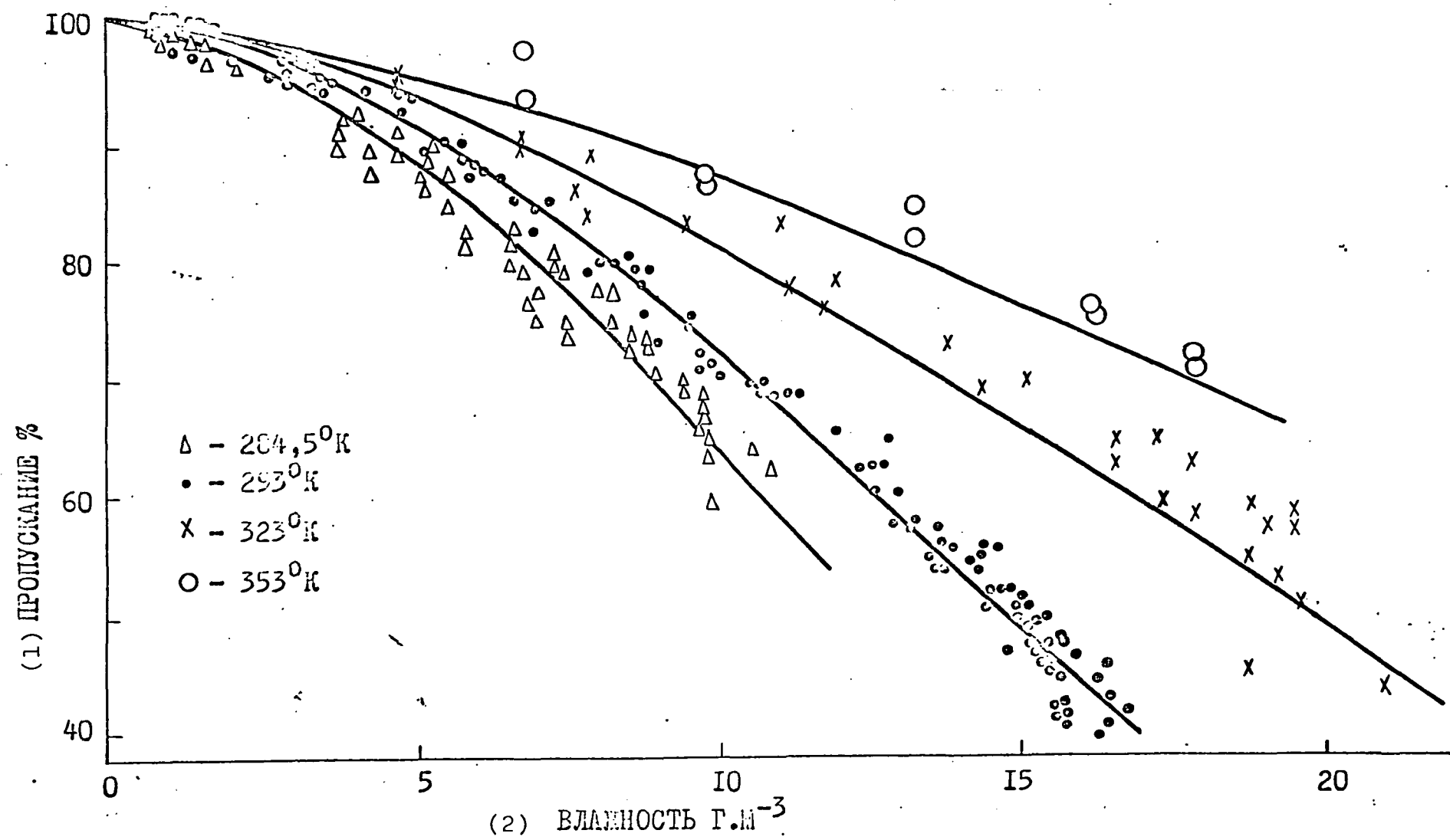


Fig. 2. Transmission of 10.6  $\mu$  radiation by pure water vapor at different temperatures. Key: (1) transmission, in %; (2) humidity, in g/m<sup>3</sup>.



$$T_{10.6} = \exp(-\tau_{10.6}) = \exp\left[-L\left[K_1 a (1 + \alpha P) + K_2 a^2 \exp(-\Delta H/R\theta)\right]\right] \quad (I)$$

where  $L$  is the course length in km,  $\theta$  is the temperature,

$a$  is the absolute humidity in  $\text{g/m}^3$ ,

$P$  is the expanding gas pressure in mbar,

$R$  is a universal gas constant, and

$K_1 = 1.76 \cdot 10^{-3} \text{ m}^3/\text{g km}$ ,  $K_2 = 0.42 \cdot 10^{-6} \text{ m}^6/\text{g}^2 \text{ km}$ ,  $\alpha = 1.78 \cdot 10^{-3} \text{ mbar}^{-1}$ , and  $\Delta H = -4546 \text{ cal/mole}$  are adjustment parameters

found by the least square method.

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A regression curve (fig. 3) shows that formula (1) describes the experimental results presented in figs. 1 and 2 and the results of additional experiments conducted at  $L=1.99 \text{ km}$ ,  $\theta=292^\circ\text{K}$ , in pure water vapor, and at  $L=2.98 \text{ km}$ ,  $\theta=340^\circ\text{K}$ , in a mixture of  $\text{N}_2+\text{H}_2\text{O}$  well (the mean square deviation  $\delta\tau=0.08$ ). Primary data of the experiments are presented in the appendix.

### Discussion of Results

The role of aerosol in  $10.6 \mu$  radiation attenuation. Technical difficulties prevented conducting direct measurements of  $10.6 \mu$  radiation scattering by an aerosol in the cell. Therefore, the role of aerosol was evaluated in regard to the ratio of radiation attenuation values at  $10.6$  and  $0.63 \mu$ . The experiments were conducted in pure water vapor at  $L=2.98 \text{ km}$  and  $\theta=311, 293$  and  $284.5^\circ\text{K}$  (fig. 4). Since water vapor practically does not absorb radiation of  $0.63 \mu$  [2], the radiation attenuation is determined by aerosol scattering. One finds from fig. 4 that the optic density ratios  $\gamma_e = \tau_{0.63}/\tau_{10.6}$  at a relative humidity  $r=75\%$  are no greater than  $0.20, 0.25$  and  $0.40$  at  $\theta=311, 293$  and  $284.5^\circ\text{K}$ , respectively. On the other hand, according to calculations [2], analogous ratios for total attenuation coefficients  $\gamma_c$  for an aerosol of the Young type with distribution of particles by sizes amount to  $10-20$ , i.e., are known to be greater than the values obtained from fig. 4. Even for a single dispersion aerosol with a particle size of approximately  $20 \mu$ , for which  $\gamma_c$  is minimal,

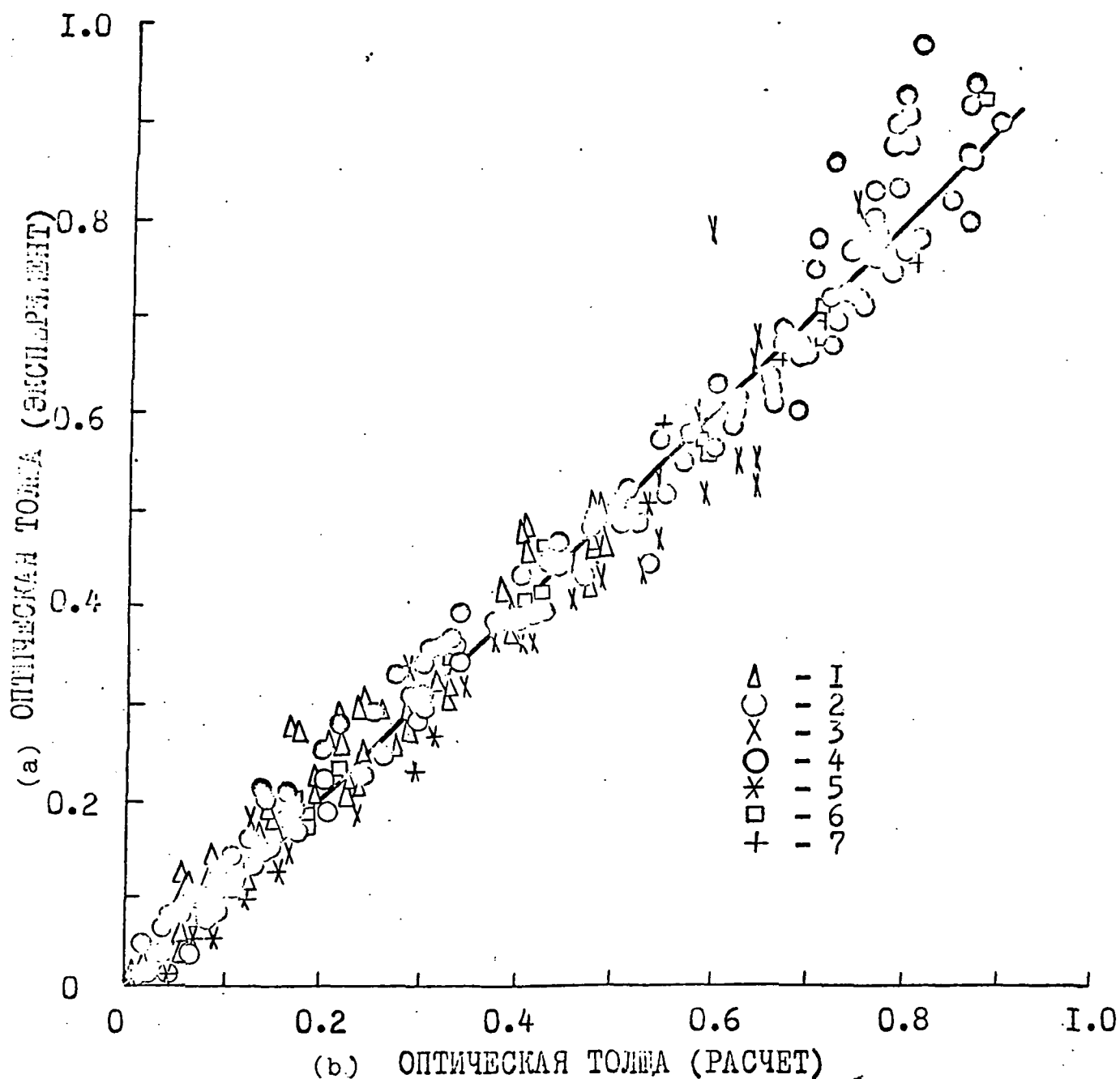


Fig. 3. Regression function (1-5, water vapor; 6 and 7, a mixture of water vapor with nitrogen; 1 -  $\theta=284.5^\circ\text{K}$ ,  $L=2.98$  km; 2 -  $=293^\circ\text{K}$ ,  $L=2.98$  km; 3 -  $=323^\circ\text{K}$ ,  $L=2.98$  km; 4 -  $=353^\circ\text{K}$ ,  $L=2.98$  km; 5 -  $=293^\circ\text{K}$ ,  $L=1.99$  km; 6 -  $=293^\circ\text{K}$ ,  $L=2.98$  km; 7 -  $=340^\circ\text{K}$ ,  $L=2.98$  km). Key: (a) optic density (experiment); (b) optic density (calculation).

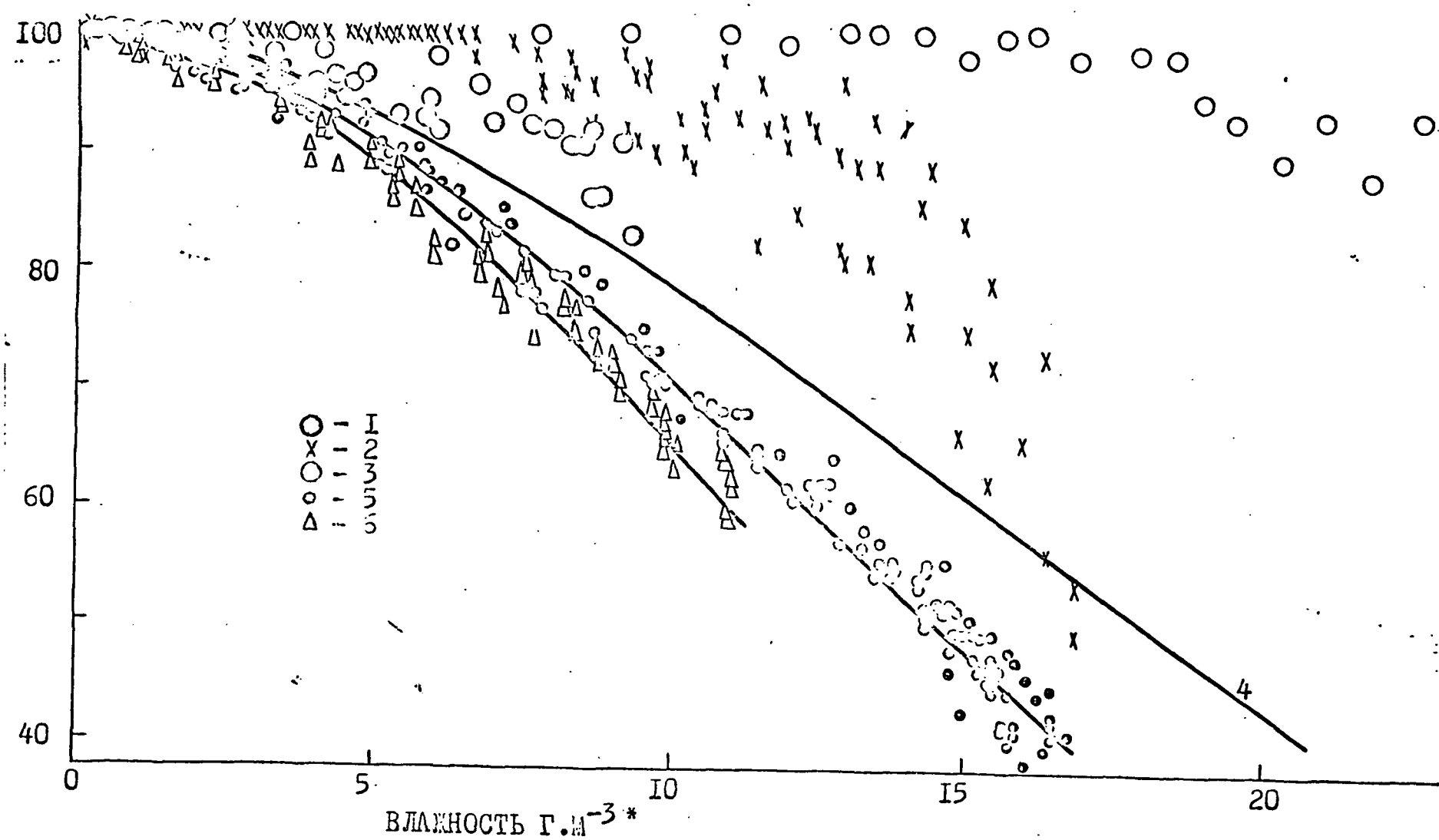


Fig. 4. Transmission of 0.63 and 10.6  $\mu$  radiation by pure water vapor (1-3, 0.63  $\mu$ ,  $\theta=311$ , 293, 284.5°K; 4-6, 10.6  $\mu$ ,  $\theta=311$ , 293, 284.5°K, respectively). \*Humidity, in  $\text{g/m}^3$ .

it amounts to 0.83, which also fails to conform to the experimental results. From a comparison of  $\gamma_e$  from fig. 4 and  $\gamma_c$  from [2], one can conclude that the contribution of water or water-containing aerosol to 10.6  $\mu$  radiation attenuation in experiments in a vessel is slight. This is even more obvious from fig. 5, /12 where the same measured values of T are shown in dependence on the relative humidity r. The dependence of  $T_{0.63}$  on r is characteristic of water or water-containing aerosol: attenuation is almost absent at  $r < 30-35\%$ , increases slightly at  $35\% < r < 75\%$ , and increases rapidly at  $r > 75\%$ . The zones of points corresponding to transmission  $T_{0.63}$  at different  $\theta$  practically overlap in this figure: a fact which reflects the basic role of relative humidity in aerosol formation processes. In contrast, the temperature has a substantial effect on  $T_{10.6}$ . This confirms the difference between attenuation mechanisms of 10.6  $\mu$  radiation, related primarily to molecular absorption, and 0.63  $\mu$  radiation, where pure scattering of the radiation on the aerosol occurs.

Fig. 5 shows that the curve of  $T_{10.6}$  calculated by (1) for  $\theta = 273^\circ\text{K}$  drops into the zone of measured values of  $T_{0.63}$ . Thus, if a smooth extrapolation of experimental results for  $T_{0.63}$  and  $T_{10.6}$  from  $\theta = 284^\circ\text{K}$  to  $\theta = 273^\circ\text{K}$  ( $\Delta\theta = 9^\circ$ ) is valid, only at negative temperatures on the Celsius scale, where molecular absorption becomes slight, can the role of large water particles in 10.6  $\mu$  radiation attenuation become significant.

Since the values of  $\gamma_c$  apply only to spherical water aerosol particles, for extending this conclusion to the conditions of an actual clear atmosphere<sup>1</sup> containing aerosol of different types, additional arguments are necessary. In connection with this, measurements of 10.6  $\mu$  radiation transmission were performed in a multiple vessel at  $\theta = 293^\circ\text{K}$  with the use of unpurified air from

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<sup>1</sup>A clear atmosphere here and elsewhere indicates stable anticyclone situations with a visibility above 20 km.

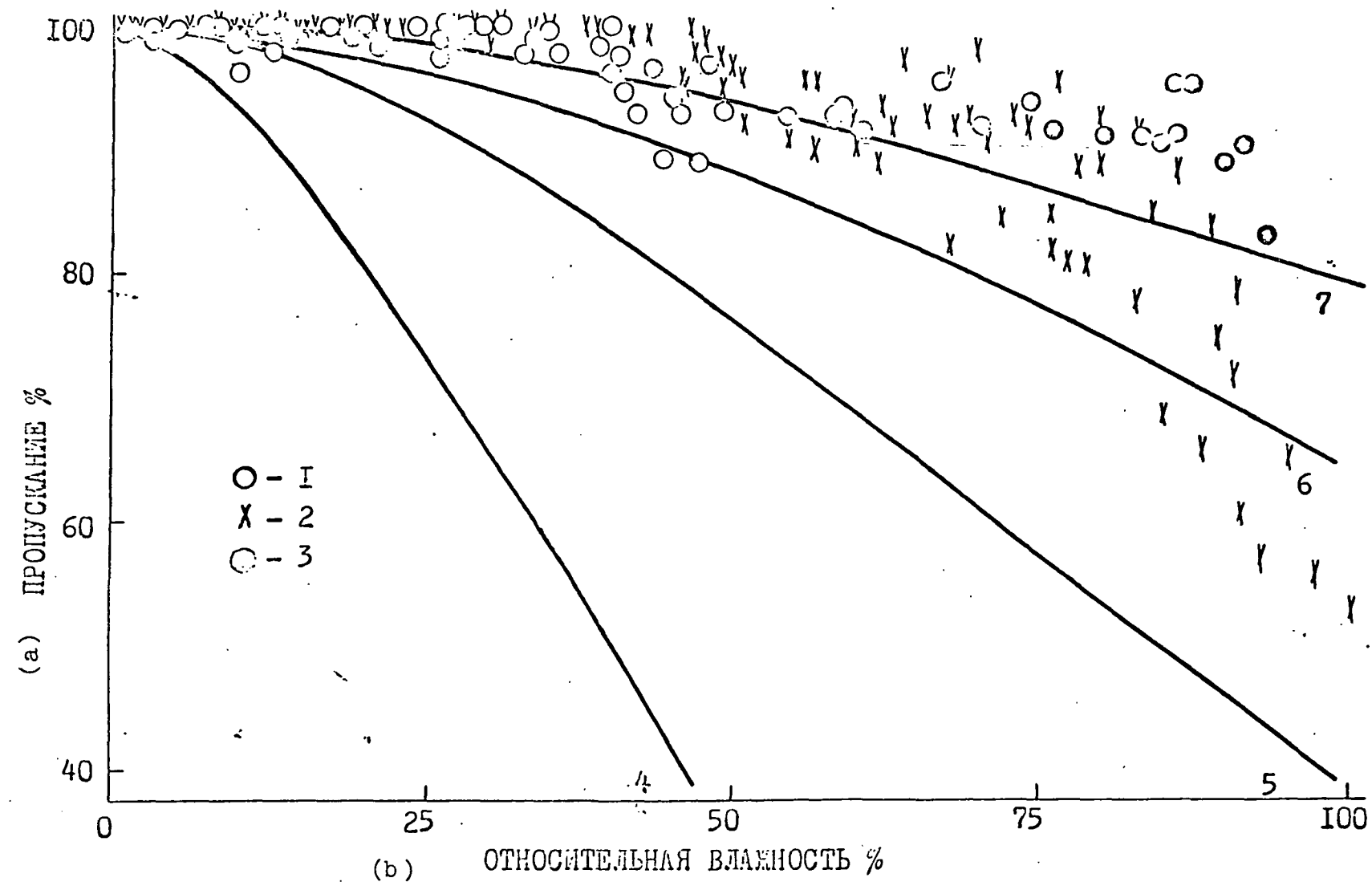


Fig. 5. Dependence of transmission of 0.63 and 10.6  $\mu$  radiation on relative humidity (1-6, the same as in fig. 4; 7, 10.6  $\mu$ ,  $\theta=273^\circ\text{K}$ ). Key: (a) transmission, in %; (b) relative humidity, in %.

the surrounding atmosphere as the expanding gas.

Table 1 presents values measured under these conditions for  $\tau_e = -\ln(T_{10.6})_{\text{air}}$  and calculated optic densities  $\tau_c = \tau_{\text{H}_2\text{O}} + \tau_{\text{CO}_2}$  ( $\tau_{\text{H}_2\text{O}}$  was calculated by formula (1), while  $\tau_{\text{CO}_2}$  was taken from [3]). As the table shows,  $\tau_e$  exceeds  $\tau_c$  only slightly (by less than 10%, on the average), and, consequently, the conclusion concerning the slight contribution of aerosol to the total 10.6  $\mu$  radiation attenuation can be extended to these experimental conditions. /14

Comparison of the results of different authors. A comparison of the results of calculation of 10.6  $\mu$  radiation transmission by water vapor for humid air with the use of approximation expressions of different researchers is presented in figs. 6 and 7. For comparability of the results, all these expressions are reduced to a common form and to a temperature of 298°K, at which the measurements of [4] were conducted, with consideration for the temperature dependence obtained in each work. The expression from [5] for  $\lambda=11.1 \mu$  was extrapolated to  $\lambda=10.6 \mu$ . The temperature dependence of [5] was used for the expression from [6]. Thus, the following formulae were obtained:

$$\begin{aligned}\tau_1 &= 8,88 \cdot 10^{-4} a^2 L \quad (\text{pure water vapor [4]}), \\ \tau_2 &= (1,76 \cdot 10^{-3} a + 8,56 \cdot 10^{-4} a^2) L \quad (\text{pure water vapor n.r.}), \\ \tau_3 &= (3,34 \cdot 10^{-6} a P + 8,88 \cdot 10^{-4} a^2) L \quad (\text{air [4]}), \\ \tau_4 &= 13,07 \cdot 10^{-4} a^2 L \quad (\text{air [5], at } K_1=0), \\ \tau_5 &= (9,86 \cdot 10^{-6} a P + 13,07 \cdot 10^{-4} a^2) L \quad (\text{air [5], at } K_1=0.1), \\ \tau_6 &= (5,46 \cdot 10^{-6} a P + 6,94 \cdot 10^{-4} a^2) L \quad (\text{air [6]}), \\ \tau_7 &= 10,76 \cdot 10^{-4} a^2 L \quad (\text{air [7]}), \\ \tau_8 &= [1,76 \cdot 10^{-3} a (1 + 1,78 \cdot 10^{-3} P) + 8,56 \cdot 10^{-4} a^2] L \quad (\text{air n.r.}),\end{aligned}$$

where  $a$  is the absolute humidity, in  $\text{g/m}^3$ ,

Table 1\*

Comparison of Experiments and Calculations  
on Air Attenuation of 10.6 Micron Radiation

1 Эксперимент						6 Расчет			8	9
$P^2$ (атм)	$a^3$ (г/м <sup>3</sup> )	$\theta^\circ K$	L (км)	$(T_{10,6})_{\text{возд.}}^4$	$\tau_{\text{э.}}^5$	$\tau_{H_2O}$	$\tau_{CO_2}$	$\tau_p^7$	$\Delta \tau = \tau_{\text{э.}} - \tau_p$	$\frac{\Delta \tau}{\tau_{\text{э.}}} (\%)$
1,0	2,18	293	2,98	0,773	0,265	0,046	0,209	0,255	0,010	4
1,0	2,92	293	2,98	0,745	0,293	0,068	0,209	0,277	0,018	6
1,0	6,74	293	2,98	0,571	0,560	0,233	0,209	0,442	0,118	21
1,0	9,22	293	2,98	0,520	0,654	0,387	0,209	0,596	0,058	9
1,0	10,23	293	1,99	0,610	0,493	0,318	0,139	0,457	0,036	7
1,0	10,32	293	1,99	0,600	0,511	0,320	0,139	0,459	0,052	10
1,0	11,26	293	2,98	0,469	0,764	0,541	0,209	0,750	0,014	2
1,0	13,04	293	2,98	0,400	0,919	0,701	0,209	0,910	0,009	1

Key: 1 - experiment; 2 - P (atmospheres); 3 - a (g/m<sup>3</sup>); 4 -  $(T_{10,6})_{\text{air}}$ ; 5 -  $\tau_{\text{э.}}$ ; 6 - calculation; 7 -  $\tau_{\text{с.}}$ ; 8 -  $\Delta \tau = \tau_{\text{э.}} - \tau_{\text{с.}}$ ; 9 -  $\Delta \tau / \tau_{\text{э.}} (\%)$ . \* [Commas in tabulated material are equivalent to decimal points]

P is the air pressure in mbar, and

L is the course length in km.

Fig. 6 presents the results of calculations of  $T = \exp(-\tau)$  for  $P = 1013$  mbar and  $L = 1$  km, the maximum course for which approximation expressions were obtained in all the works except this one (the curve numbers conform to the indices of  $\tau$ ). Fig. 6 shows that within the limits of accuracy of the experiments, the results of calculations by all the formulae are in satisfactory agreement, if the data of [5] (curve 5) at  $K_1 = 0.1$  are

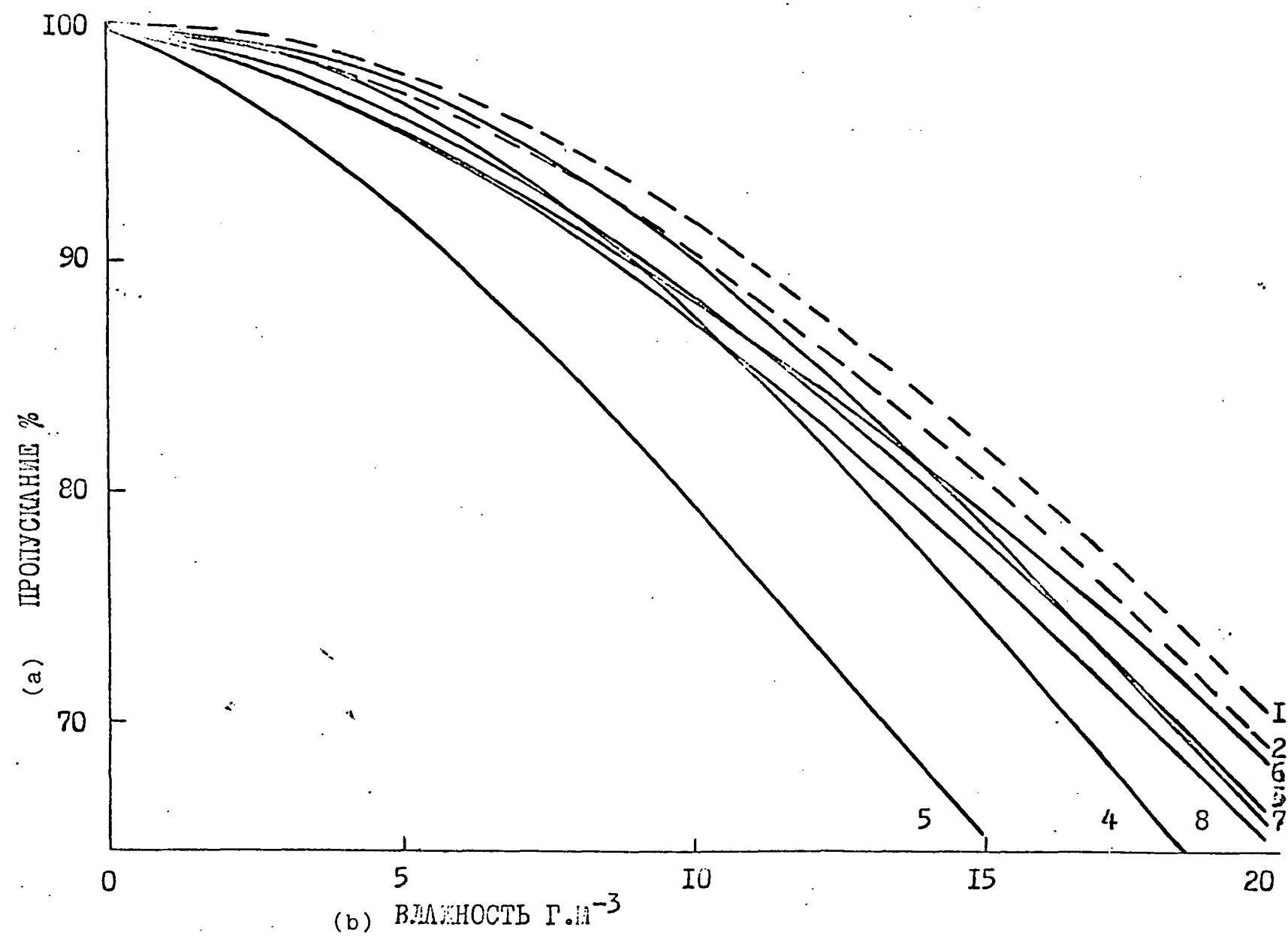


Fig. 6. Comparison of results of laboratory experiments for a course of 1 km. Key: (a) transmission, in %; (b) humidity, in g/m<sup>3</sup>.



excluded.<sup>2</sup> However, if the results of all the works are extrapolated to  $L=3$  km, the maximum trajectory of this study, discrepancies in the values of radiation transmission by humid air can reach 25-30% at high humidities.

Comparison of the results of laboratory and full-scale measurements. The authors of most full-scale measurements of solar radiation attenuation by the entire thickness of the atmosphere perform only a qualitative comparison of their results to the data of laboratory experiments. A quantitative approach to comparison full-scale and laboratory results, consisting of integration of expression (1) in regard to the path of the ray at meteorological parameter values measured simultaneously in each full-scale experiment, was presented in [8] and developed in [9-14]. In this approach, it proved necessary to take into consideration not the overall water vapor concentration  $w$  in a column of the atmosphere but the actual altitude profiles of humidity, temperature and pressure. Expression (1) is directly applicable only for calculations of attenuation in a narrow section of the spectrum in the vicinity of  $10.6 \mu$ . One can assume, however, that  $\tau_c(\lambda)=C(\lambda)\tau_{10.6}$ , since approximately the same temperature dependence [12] occurs in all the microwindows of the 8-13  $\mu$  region. The results of [7] were used for determining the value of the standardizing factor  $C(\lambda)$  (table 2).

Further analysis employs the results of measurements of solar radiation attenuation by the entire thickness of the atmosphere obtained in the middle latitudes (the Moscow region and the Black Sea coast) and in the Antarctic and the data of works [15-17] for the Moscow area and the tropics, selected for cases dealing with a clear atmosphere. The calculations took into consideration humidity, temperature and pressure profiles measured at aerological stations nearest the points at which the

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<sup>2</sup>The value of  $K_1$  was carelessly defined in [5]: in the text,  $K_1=0$ ; in fig. 8,  $K_1=0.1$ .

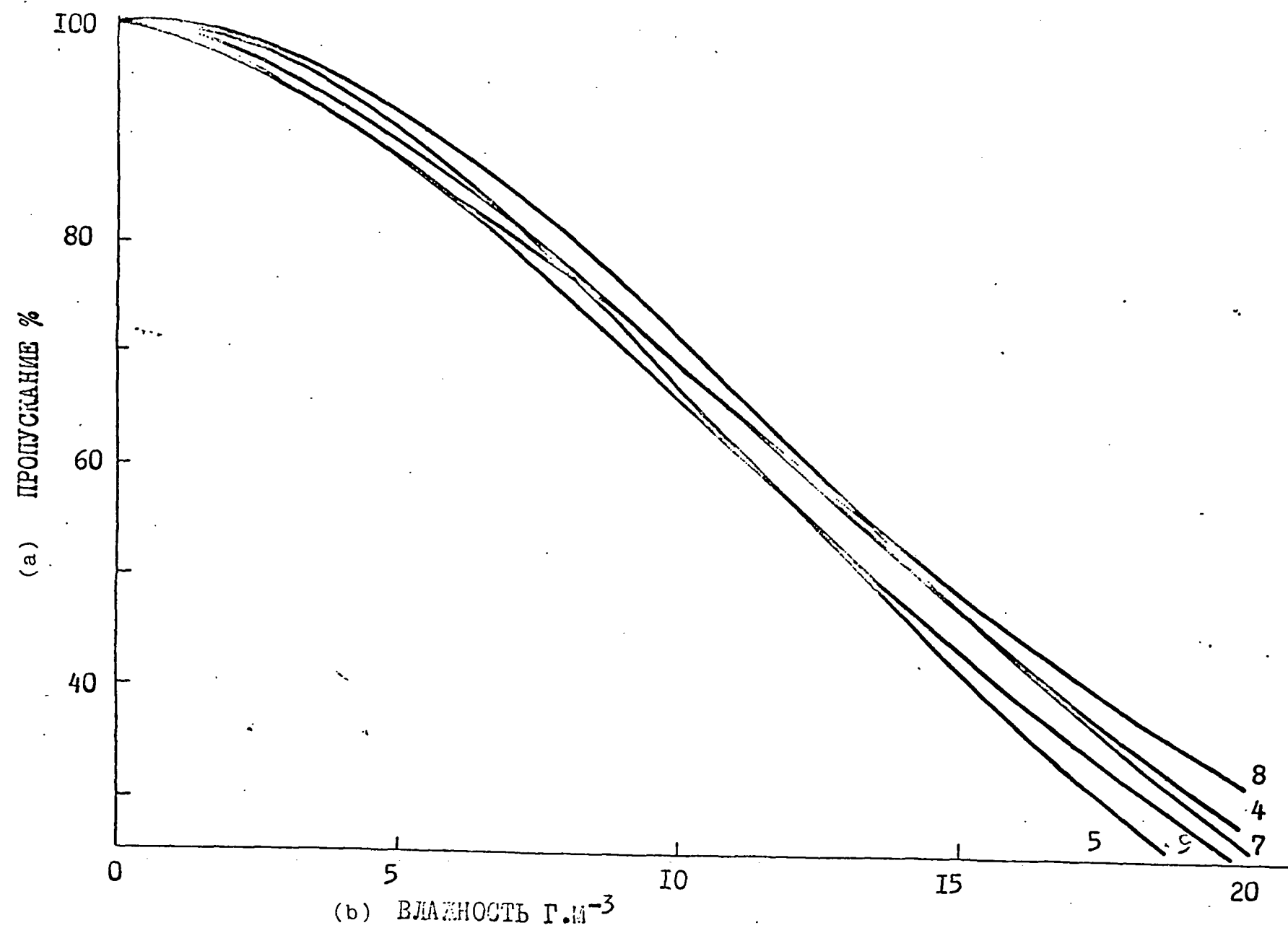


Fig. 7. Comparison of results of laboratory experiments for a course of 3 km. Key: (a) transmission, in %; (b) humidity, in g/m<sup>3</sup>.

Table 2\*

## Standardizing Factor Values

$\lambda$ x MICM	$C(\lambda)$	$\lambda$ x MICM	$C(\lambda)$	$\lambda$ x MICM	$C(\lambda)$
8,10	0,59	10,40	0,95	12,40	1,80
8,30	0,59	10,60	1,00	12,50	1,90
8,60	0,62	11,10	1,12	12,80	2,10
8,74	0,63	11,60	1,29	12,90	2,20
9,06	0,67	11,80	1,37	13,00	2,25
10,15	0,85	12,20	1,59	13,10	2,30

Key: x - microns. \*[Commas in tabulated material are equivalent to decimal points.]

full-scale experiments were conducted.

In fig. 8, calculations by (1) with consideration for the standardizing factor  $C(\lambda)$  are compared to the entire collection of full-scale experimental data for the 10-13  $\mu$  region. The results are represented both in the form of a regression function and in the form of a dependence of  $\tau_e/\tau_c$  on  $\tau_c$ . The ratio of  $\tau_e/\tau_c$  should be equal to one in a case where only molecular absorption plays a role under natural conditions. The ratio should increase with a significant role of aerosol or other factors not taken into consideration by (1). As fig. 8 shows, this ratio actually is equal to one with a dispersion of 0.15 in a broad range of  $0.05 < \tau < 1$ . It is important to note that this occurs for all the wavelengths considered and for all the observation points. Thus, in all these cases under natural conditions, molecular absorption is the main cause of radiation attenuation.

At  $\tau < 0.05$ , which corresponds to winter conditions in the

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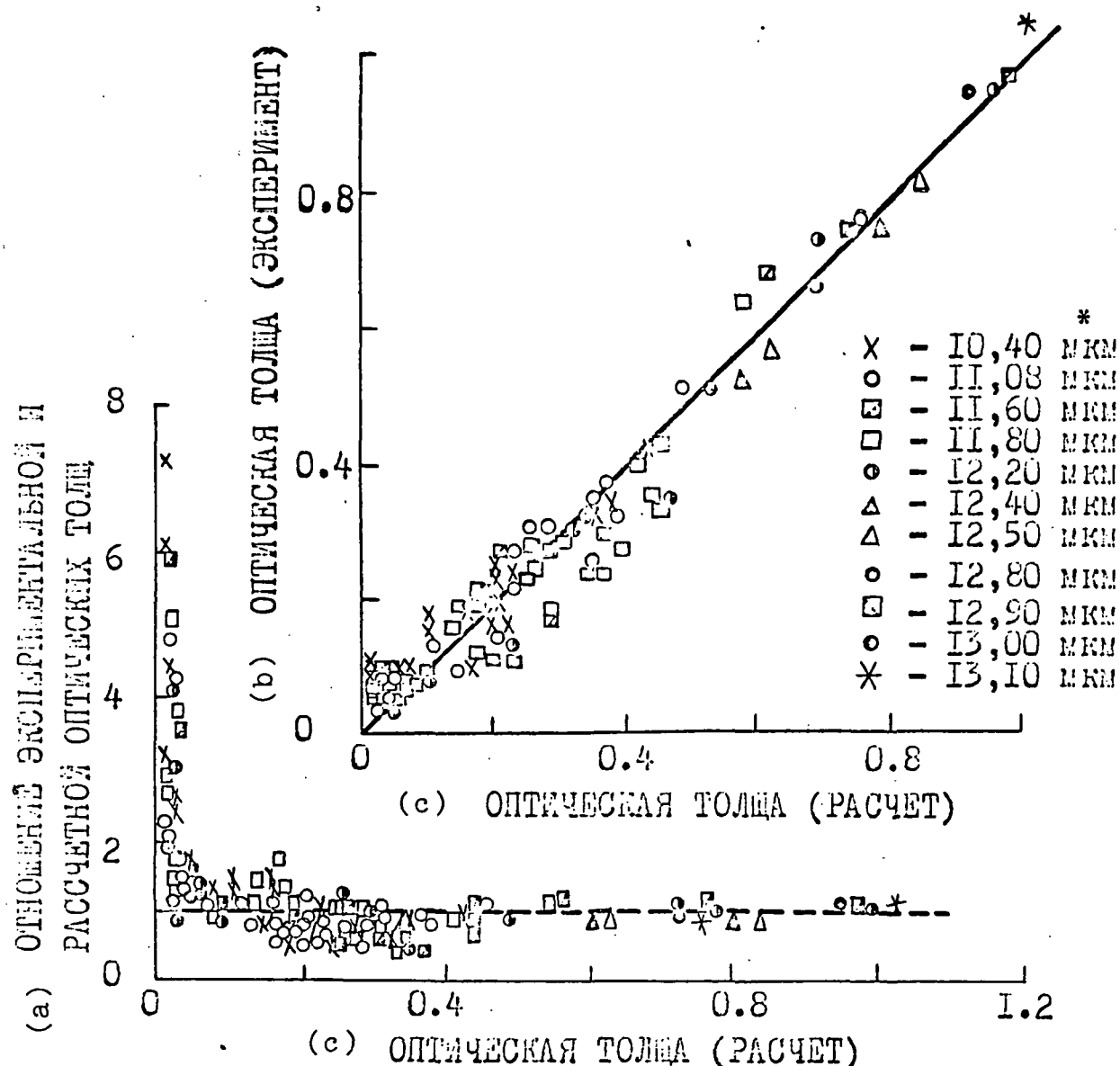


Fig. 8. Comparison of full-scale measurement results to calculations by (1). Key: (a) ratio of experimental and calculation optic density values; (b) optic density (experiment); (c) optic density (calculation). \*Microns.

middle latitudes, the ratio  $\tau_e/\tau_c$  increases substantially, indicating the need for injecting an additional radiation attenuation mechanism for accounting for the "excess" optic density. This "excess" optic density hypothetically can be related to both radiation scattering by large aerosol particles [13] and radiation absorption by a finely dispersed aerosol fraction [18].

For evaluating the applicability of (1) at low humidities and low temperatures, measurements of the attenuation of solar radiation in the 8-13  $\mu$  transparency window of the atmosphere were conducted on the Twenty-third Soviet Antarctic Expedition (1977-1978). These measurements were accompanied by constant observation of the spectral transparency of the entire mass of the atmosphere at a wavelength of 0.63  $\mu$ . The value of the vertical optic density for  $\lambda=0.63$   $\mu$  under the conditions of these measurements was  $\tau_{0.63}=0.048-0.100$  (an average value of 0.064). This value is 10 to 20% higher than Rayleigh scattering ( $\tau_{\text{Ray}}=0.054$  and 0.059 according to [19] and [20], respectively), which makes it possible to consider the measurement conditions as conforming to a practically "aerosol-free" atmosphere. The results of measurements in the Antarctic are presented in fig. 9, from which it follows directly that calculated  $\tau_c$  and measured optic density values  $\tau_e$  are in agreement within the limits of error of the measurements for microwindows in the range 10.4-12.7  $\mu$ . The mean square deviation from a straight line corresponding to  $\tau_e=\tau_c$  amounts to 0.007 for the entire collection of data in this section of the spectrum.

An important fact which follows from fig. 9 is the  $\tau_e$  value's distinctly exceeding  $\tau_c$  for microwindows in the 8-10  $\mu$  range. Since the aerosol attenuation was negligibly slight in these measurements, the additional absorption is known to be molecular.

Thus, comparison of calculations by (1) to the results of full-scale measurements demonstrated that accounting for molecular absorption is necessary in all situations in a clear atmosphere. In the 10-13  $\mu$  region, expression (1) with consideration for  $C(\lambda)$  completely describes the data of full-scale measurements during the warm period of the year. The contribution of aerosol attenuation must also be considered under winter conditions and in a cloudy atmosphere.

The mechanism of attenuation of 10.6  $\mu$  radiation by the

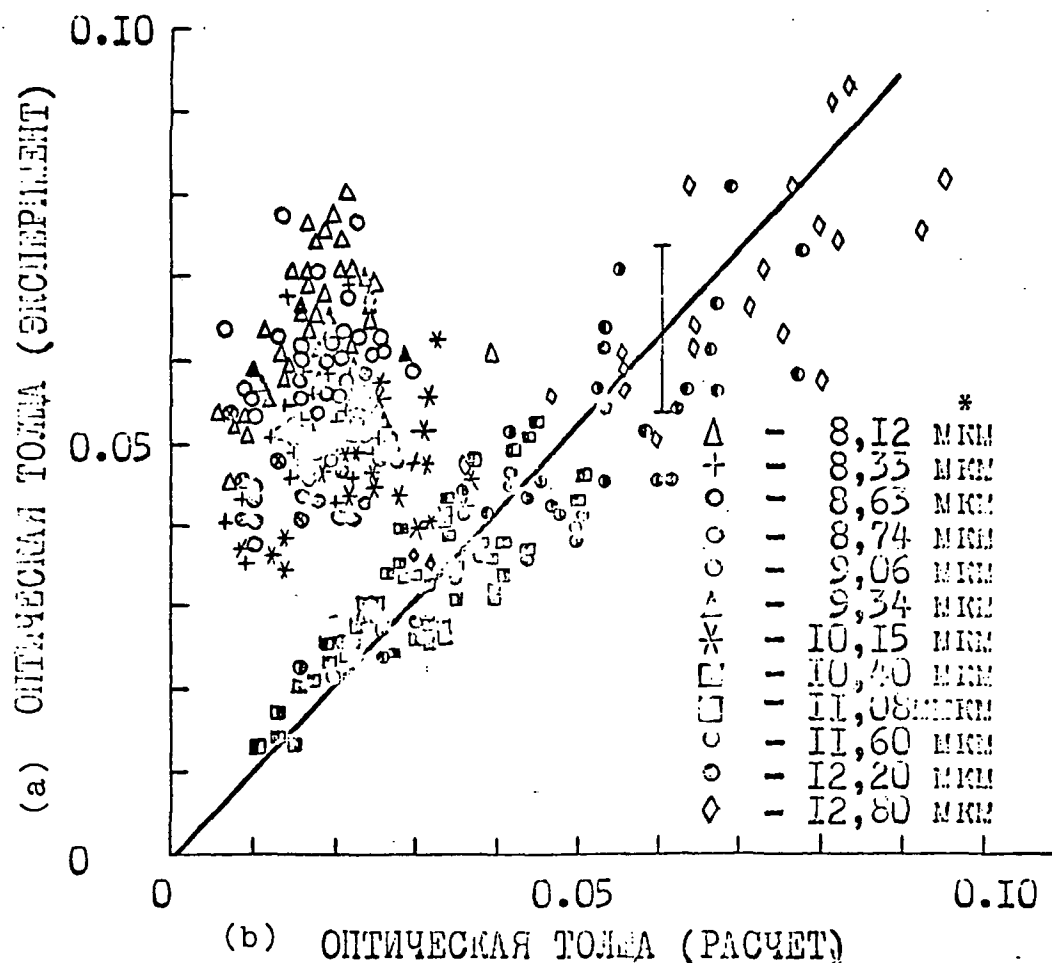


Fig. 9. Comparison of the results of full-scale measurements in the Antarctic to calculations by (1) (the vertical line represents the boundary of experimental errors). Key: (a) optic density (experiment); (b) optic density (calculation); \*microns.

water vapor continuum. It has been demonstrated above that the attenuation in question cannot be attributed to water or water-containing aerosol, and that its main cause is molecular absorption. Works [5] and [21] expressed the hypothesis that this molecular absorption is conditioned by two mechanisms acting at once. One of them is defined by the remote wings of strong lines and bands of absorption of water vapor with centers in the vicinity of  $6.3 \mu$  and beyond  $14 \mu$ . These wings are formed due to collisions of  $H_2O$  molecules with other air molecules, primarily nitrogen. The other mechanism is involved with water

vapor dimer molecules. A number of facts observed in this study support such a hypothesis.

The first important circumstance is the fact that the injection of significant amounts ( $P_{N_2} \gg 50 P_{H_2O}$ ) of an extraneous gas into the cell only slightly influences the value of  $T$ . This indicates that the deformation of water vapor absorption lines related to their impact expansion by nitrogen, as well as by air, has a slight influence on the transparency of the mixture. It follows that the contribution of the line component of the spectrum is slight in itself, and that the magnitude of the absorption in question is determined practically completely by the scattered component of molecular absorption. Since the collision diameters for self-expansion and expansion by nitrogen differ by less than an order [22], one can also conclude that the quadratic dependence of  $\tau_{10.6}$  on a observed - approximation formula (1) - cannot be related to the deformation of the wings of  $H_2O$  monomer lines in self-expansion, even in experiments with pure water vapor. /24

The second essential feature is the extremely sharp "negative" temperature dependence of  $\tau_{10.6}$ . It can be demonstrated that the second term in (1) varies with the temperature as  $\theta^{-7.4}$ , which is substantially steeper than  $\theta^{-n}$  at  $n=0.5$  to  $2.0$ : the values encountered in a description of the temperature deformation of the line contours. This can be considered as support for the idea that the temperature course of  $\tau_{10.6}$  basically reflects the variation in the number of absorbing particles.

To summarize, one can suppose that the attenuation under consideration is determined primarily by the scattered spectrum of molecular absorption, which is not distorted by the extraneous gas. At a high humidity level, its intensity increases in proportion to the square of the humidity and decreases with an increase in the temperature at a rate whose modulus exceeds the characteristic values for temperature deformation of individual line contours and for pre-exponential factors in expressions for the distribution of particles by levels. It seems logical

to attribute this spectrum to water vapor dimers, whose concentration at low concentrations is practically proportionate to the square of the absolute humidity  $a$ . Based on an equation of the equilibrium between quantities of monomers and dimers at low concentrations of the latter, the value of the measured optic density at a wavelength  $\lambda$  can be recorded in such a situation as

$$\tau(\lambda) = K_1^* a B_1(\theta) + K_2^* a^2 B_2(\theta) \exp(-\Delta E/R\theta), \quad (2)$$

where  $K_1^*$  and  $K_2^*$  are coefficients related to the intensities in monomer and dimer spectra;  $\Delta E$  is the energy of dimer formation;  $B_1(\lambda)$  and  $B_2(\lambda)$  are functions which define the relative temperature variations of intensities in the monomer and dimer spectra, respectively. The dependence (2) obviously can be approximated by formula (1), where only the second member depends on the temperature, with a known error. Since the contribution of "monomer" line absorption is slight, as demonstrated above, it can be neglected entirely in (2) at average and high humidities  $a$ ; therefore, the effect of  $B_1$  on the parameters of expression (1) need not be taken into consideration. With respect to  $B_2$ , this temperature dependence can be considered weak, on the one hand, due to the known low energy of the bottom level of  $(H_2O)_2$  dimers and the low value of the energy of their dissociation ( $\Delta E = 3-6$  kcal/mole [23, 24]) and, on the other, due to the low sensitivity of the form of diffusion bands to temperature changes.<sup>3</sup> Thus, one can assume that the value of  $\Delta E$  in expression (2) will primarily determine the value of the adjustment parameter  $\Delta H$  in (1). This makes it possible to impart to the value found,  $\Delta H = -4.5$  kcal/mole, the sense of an estimate of the dimer formation energy value. Further refinement of this estimate can

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<sup>3</sup>Calculations [24] actually demonstrate quite slight distortion of the contours of rotation and rotation-oscillation bands of the dimers from the temperature in a variation range of interest to us (figs. 4-7 of the work cited).



be achieved by correction for the temperature dependence of the statistical sum in regard to rotation states of the dimer; this dependence is proportionate to  $\theta^{-3/2}$ . With account for the total temperature dependence referred to above for the second term in (1),  $\theta^{-7.4}$ , this produces  $\Delta H = -3.6$  kcal/mole. Both these values conform well to the range of values of  $\Delta E$  [23, 24].

Unfortunately, specifying the character of transitions responsible for the absorption under discussion is difficult due to incompleteness of the theoretical analysis of the  $(H_2O)_2$  spectrum, although in [25] this absorption is tentatively attributed to a translation-oscillation transition of the dimer, while in [26] it is attributed to a libration transition.

/26

In theoretical study [27], the experimental facts observed are explained by the interaction of radiation with pairs of nearly colliding identical absorbing molecules, with consideration for their configurations and potentials. Based on the fact that undisturbed wave functions of colliding molecules are used in solving the Schroedinger equation, the authors of [27] attribute the spectrum in question to the remote wings of absorption bands of monomer water molecules. However, from our point of view, accounting for weak disturbances of wave functions hardly leads to radical qualitative changes in the results, and a pair of nearly colliding molecules at the moment of interaction with radiation can be considered as a short-lived weakly bound dimer. Therefore, differences of opinion between the authors of [27] and the advocates of the dimer hypothesis may prove more apparent than real.

### Conclusions

Brief conclusions from the research conducted useful for satellite meteorology and for solving a number of other practical problems can be formulated as follows:

1. Continuous absorption of radiation by water vapor must be taken into consideration in all the atmospheric situations

encountered. A calculation procedure based on expression (1), which rests on data of laboratory experiments, can be used successfully for reliable estimates of continuous absorption in a spectral region.

2. Under clear weather conditions (stable anticyclone situations with a visibility greater than 20 km) during the warm part of the year, only molecular absorption need be taken into consideration for estimates of the total attenuation of the atmosphere in narrow sections of the spectrum of 10-13  $\mu$  which are free of selective absorption lines. /27

3. Under winter conditions, when the contribution of molecular absorption becomes extremely slight due to the low water vapor concentration in the atmosphere, and under cloudly atmospheric conditions, the contribution of aerosol can become substantial. In this case, one must give attention to both the possibility of radiation scattering on coarsely dispersed aerosol particles in certain situations and the possibility of radiation absorption by submicron aerosol particles in other situations.

4. Additional molecular absorption, which can be related both to a stronger effect of the water vapor absorption band with a center at 6.3 microns and to the effects of other small gas components of the atmosphere, must be taken into consideration in the microwindows of the 8-10  $\mu$  spectrum range.

## REFERENCES

1. Aref'yev, V. N., O. A. Volkovitskiy, N. V. Goncharov and V. I. Dianov-Klokov, "Opticheskaya mnogokhodovaya kyuveta dlya issledovaniya pogloshcheniya iskusstvennymi atmosferami [A Multichannel Optic Cell for Studying Absorption with Artificial Atmospheres]," PTE, 1, 198-201 (1974).
2. Zel'manovich, I. L. and K. S. Shifrin, Tablitsy po svetorasseyaniyu [Light Diffraction Tables], Gidrometeoizdat, Leningrad, Vol. III, 1968, Vol. IV, 1971.
3. Aref'yev, V. N. and N. I. Sizov, "Rezonansnoye pogloshcheniye izlucheniya CO<sub>2</sub>-lazera uglekislym gazom [Resonance absorption of CO<sub>2</sub> laser radiation by carbon dioxide]," Kvantovaya elektronika, 4/6, 1361-1364 (1977).
4. McCoy, J. H., D. B. Rensch and R. K. Long, "Water vapour continuum absorption of carbon dioxide laser radiation near 10 $\mu$ ," Appl. Opt. 8/7, 1471-1478 (1968).
5. Bignell, K. J., "The water vapour infrared continuum," Quart. J. Roy. Meteorol. Soc. 96/409, 390-403 (1970).
6. Shumate, M. S. et al., "Water vapor absorption of carbon dioxide laser radiation," Appl. Opt. 15/10, 2480-2488 (1976).
7. Burch, D. E., "Investigation of the absorption of infrared radiation by atmospheric gases," Semi-annual technical report U-4784, contract NF 19628-69-C-0263, 1970.
8. Dianov-Klokov, V. I. and V. M. Ivanov, "O mekhanizme pogloshcheniya lazernogo izlucheniya s  $\lambda=10.6$  mkm vodyanym parom v atmosfere [The Mechanism of Laser Radiation Absorption with a Wavelength of 10 Microns by Water Vapor in the Atmosphere]," Kvantovaya elektronika 2/7, 1579-1581 (1975).
9. Aref'yev, V. N. and V. I. Dianov-Klokov, "K otsenke vliyaniya meteorologicheskikh faktorov na oslableniye lazernogo izlucheniya 10.6 mkm continuumom vodyanogo para v chistoy atmosfere [Evaluation of the Effects of Meteorological Factors on the Attenuation of 10.6 Micron Laser Radiation by the Water Vapor Continuum in a Clear Atmosphere]," Kvantovaya elektronika 3/4, 923-925 (1976).
10. Aref'yev, V. N. and V. I. Dianov-Klokov, "K sopostavleniyu model'nykh i naturnykh izmereniy pogloshcheniya v okne prozrachnosti atmosfery 8-13 mkm [Comparison of Model and Full-Scale Measurements of Absorption in the 8-13 Micron

Atmospheric Transparency Window]," Trudy IEM, 4(61), 18-21 (1976).

11. Aref'yev, V. N. and V. I. Dianov-Klokov, "Oslableniye izlucheniya 10.6 mkm vodyanym parom i rol' dimerov ( $H_2O$ )<sub>2</sub> [Attenuation of 10.6 Micron Radiation by Water Vapor and the Role of ( $H_2O$ )<sub>2</sub> Dimers]," Optika i spektroskopiya 42/5, 849-855 (1977).
12. Dianov-Klokov, V. I., V. M. Ivanov and Yu. A. Savitskiy, "O vliyaniy assotsiatov molekul vody na oslableniye sveta v 'okne prozrachnosti' atmosfery 8-13 mkm [The Effect of Water Molecule Associates on Light Attenuation in the 8-13 Micron Atmospheric Transparency Window]," Izv. AN SSSR, ser. FAO 11/12, 1246-1253 (1975).
13. Dianov-Klokov, V. I. and V. M. Ivanov, "O vozmozhnoy roli aerolya v oslablenii lazernogo izlucheniya  $\lambda=10.6$  mkm slabozamutnennoy atmosferoy v zimnikh usloviyakh [The Possible Aerosol Role in the Attenuation of Laser Radiation with a Wavelength of 10.6 Microns by a Slightly Cloudy Atmosphere under Winter Conditions]," Izv. AN SSSR, ser. FAO 14/3, 328-330 (1978).
14. Dianov-Klokov, V. I. and V. M. Ivanov, "Ob oslablenii radiatsii 8-13 mkm vodyanym parom pri razlichnykh meteouusloviyakh [Attenuation of 8-13 Micron Radiation by Water Vapor under Different Meteorological Conditions]," Izv. AN SSSR, ser. FAO 14/8, 847-854 (1978).
15. Malkevich, M. S., Yu. S. Georgiyevskiy, G. V. Rozenberg, A. Kh. Shukurov and A. I. Chavro, "O prazrachnosti atmosfery v IK-oblasti spektra [Transparency of the Atmosphere in the Infrared Region of the Spectrum]," Izv. AN SSSR, ser. FAO 9/12, 1257-1268 (1973).
16. Shukurov, A. Kh., M. S. Malkevich and A. I. Chavro, "Eksperimental'noye issledovaniye zakonornostey spektral'nogo propuskaniya radiatsii vertikal'nym stolbom atmosfery [Experimental Study of the Radiation Transmission by a Vertical Column of the Atmosphere]," Izv. AN SSSR, ser. FAO 12/3, 264-271 (1976).
17. Shukurov, A. Kh., Yu. S. Georgiyevskiy, A. I. Marchenkov and Ye. I. Prokhorov, "Ustanovka dlya issledovaniy spektral'nogo propuskaniya atmosfery v infrakrasnoy oblasti s borta sudna [A Device for Study of the Spectral Transmission of the Atmosphere in the Infrared Range from Aboard a Ship]," Trudy Mezhdudomstvennoy ekspeditsii TROPEKS-74 [Proceedings of the TROPEKS-74 Interdepartmental Expedition], Vol. I, Gidrometeoizdat, Leningrad, 1976, pp. 614-621.

18. Rozenberg, G. V., Yu. S. Georgiyevskiy, V. N. Kapustin, Yu. S. Lyubovtseva, A. P. Orlov, S. M. Pirogov and A. I. Chavro, "Submikronnaya fraktsiya aerolya i pogloshcheniye sveta v okne prozrachnosti 8-12 mkm [The Submicron Aerosol Fraction and Light Absorption in the 8-12 Micron Transparency Window]," Izv. AN SSSR, ser. FAO 13/11, 1185-1192 (1977).
19. Gudi, R. M., Atmosfernaya radiatsiya [Atmospheric Radiation], "Mir" Publishers, Moscow, 1966.
20. Zuyev, V. Ye., "Rasprostraneniye vidimyykh i infrakrasnykh voln v atmosfere [Propagation of Visible and Infrared Waves in the Atmosphere]," Sovetskoye radio, Moscow, 1970, p. 277.
21. Varansi, P. Chou, S. and S. S. Penner, "Absorption coefficient for water vapour in the 600-1000  $\text{cm}^{-1}$  region," J. Quant. Spectr. Rad. Transf. 8/8, 1541-1547 (1968).
22. Burch, D. E., W. L. France and D. Williams, "Total absorptance of water vapour in infrared," Appl. Opt. 2/6, 585-589 (1963).
23. Yukhnovich, G. V., Infrakrasnaya spektroskopiya vody [Infrared Spectroscopy of Water], Nauka, Moscow, 1973.
24. Braun, Ch. and A. Leidecker, "Rotation and vibration spectra for the  $\text{H}_2\text{O}$  dimer: Theory and comparison with experimental data," J. Chem. Phys. 61/8(1), 3104-3114 (1974).
25. Viktorova, A. A. and S. A. Zhevakin, "Linii vrashchatel'nogo spektra dimerov vodyanogo para v verkhney termosfere [Lines of the Rotation Spectrum of Water Vapor Dimers in the Upper Thermosphere]," Izv. AN SSSR, ser. FAO 9/2, 145-154 (1973).
26. Wolynes, P. G. and R. E. Roberts, "Molecular interpretation of the infrared water vapour continuum," Appl. Opt. 17/10, 1484-1486 (1978).
27. Nesmelova, L. I., S. D. Tvorogov and V. V. Fomin, Spektroskopiya kryl'yev liniy [Spectroscopy of Line Wings], Nauka, Novosibirsk, 1977.

Table 1

Transmission of 10.6 micron radiation by pure water vapor at a temperature of 284.5°K on a course of 2.98 km.

a	T%	b	a	r/ <sub>M</sub> <sup>3</sup>	a	T%	b	a	r/ <sub>M</sub> <sup>3</sup>	a	T%	b	a	r/ <sub>M</sub> <sup>3</sup>
98,9			0,80		85,9			5,30		76,6			8,38	
99,5			0,80		86,8			5,30		74,5			8,38	
98,I			I,0I		88,7			5,43		7I,9			8,75	
99,5			I,0I		87,7			5,43		72,6			8,75	
98,5			I,II		86,8			5,70		72,0			9,02	
99,0			I,II		84,6			5,70		72,6			9,02	
97,9			I,54		80,7			6,00		70,I			9,08	
97,9			I,54		82,5			6,00		69,8			9,08	
95,8			I,7I		80,8			6,77		69,6			9,65	
98,0			I,7I		79,5			6,77		68,3			9,65	
96,4			2,25		82,8			6,9I		65,0			9,89	
95,8			2,25		8I,3			6,9I		66,9			9,89	
94,3			3,42		76,0			7,04		66,I			9,9I	
93,7			3,42		78,3			7,04		67,8			9,9I	
88,9			3,92		76,9			7,24		63,2			IO,0I	
90,2			3,92		74,3			7,24		64,6			IO,0I	
9I,8			4,06		80,4			7,54		64,0			IO,89	
92,3			4,06		79,3			7,54		64,I			IO,89	
92,0			4,22		78,5			7,58		59,3			IO,99	
92,I			4,22		78,6			7,58		59,I			IO,99	
88,7			4,42		73,9			7,74		62,0			II,09	
86,5			4,42		73,2			7,74		6I,7			II,09	
89,2			4,86		77,0			8,2I						
90,5			4.86		76.8			8.2I						

Key: (a) transmission, in %; (b) absolute humidity, in g/m<sup>3</sup>.

[Commas in all tabular material in the Appendix are equivalent to decimal points.]

Table 2

Transmission of 10.6 micron radiation by pure water  
vapor at a temperature of 293°K on a course of 2.98 km.

a T%	b $\alpha$ $\Gamma/M^3$	a T%	b $\alpha$ $\Gamma/M^3$	a T%	b $\alpha$ $\Gamma/M^3$
I	2	I	2	I	2
100,0	0,30	96,0	2,77	87,5	6,11
100,0	0,59	96,7	2,87	86,8	6,20
99,6	0,59	97,3	3,15	82,1	6,33
99,4	0,60	95,0	3,16	86,9	6,41
99,5	0,70	96,8	3,16	84,5	6,51
98,6	0,79	96,0	3,25	82,2	6,80
100,0	0,89	93,3	3,35	83,8	6,89
100,0	0,99	95,3	3,36	82,9	7,02
100,0	1,09	94,0	3,44	84,9	7,19
99,8	1,09	97,4	3,46	83,6	7,28
98,9	1,19	93,2	3,75	80,8	7,50
97,0	1,28	92,7	3,94	78,4	7,52
97,9	1,50	94,6	4,14	78,4	7,70
97,6	1,58	91,6	4,23	76,5	7,81
99,1	1,58	93,1	4,25	79,4	7,99
99,0	1,67	94,0	4,75	79,5	8,17
96,8	1,87	92,4	4,75	80,0	8,47
99,7	1,88	93,5	4,92	77,4	8,60
99,5	1,88	90,6	5,02	74,7	8,68
99,0	1,98	88,7	5,03	78,9	8,76
98,0	2,08	89,8	5,22	72,3	8,90
96,0	2,17	88,0	5,22	74,0	9,25
97,0	2,27	90,3	5,43	75,0	9,45

Table 2  
Continuation

I	:	2	:	I	:	2	:	I	:	2
95,I		2,76		90,2		5,73		73,3		9,56
95,4		2,76		86,7		5,82		71,3		9,57
95,9		2,76		88,5		5,84		70,5		9,67
96,9		2,77		88,I		5,9I		70,6		9,78
73,4		9,79		56,7		I2,92		46,7		I5,23
70,0		9,92		59,8		I3,05		48,7		I5,3I
67,5		I0,I8		56,4		I3,25		46,2		I5,3I
68,5		I0,54		57,7		I3,28		44,9		I5,40
69,I		I0,55		54,I		I3,49		49,0		I5,46
69,I		I0,55		53,I		I3,62		43,8		I5,49
68,2		I0,66		56,9		I3,64		46,3		I5,52
68,2		I0,66		53,7		I3,84		46,8		I5,53
68,7		I0,68		53,3		I4,34		45,7		I5,54
68,4		I0,93		54,4		I4,37		46,2		I5,55
66,2		I0,97		55,0		I4,37		4I,4		I5,66
65,0		I0,97		5I,0		I4,38		40,6		I5,69
68,0		II,22		50,0		I4,4I		47,5		I5,75
68,0		II,32		50,7		I4,43		43,8		I5,76
64,I		II,45		5I,6		I4,63		39,6		I5,80
63,4		II,52		55,I		I4,67		47,0		I5,85
64,5		II,54		5I,3		I4,80		40,4		I5,85
64,8		II,87		47,8		I4,80		4I,5		I5,88
6I,4		I2,04		5I,7		I4,82		37,7		I6,03
60,5		I2,06		46,0		I4,83		45,7		I6,04
6I,7		I2,43		49,I		I4,88		44,2		I6,30



Table 2  
Conclusion

I	:	2	:	I	:	2	:	I	:	2
60,7		I2,45		5I,0		I4,97		39,2		I6,35
59,4		I2,5I		49,2		I5,03		4I,9		I6,53
6I,8		I2,60		42,4		I5,03		44,9		I6,54
62,0		I2,70		50,2		I5,I0		42,0		I6,54
64,3		I2,80		48,6		I5,I9		40,0		I6,54
								40,7		I6,83

Key: (a) transmission, in %; (b) absolute humidity, in  $\text{g/m}^3$ .

Table 3

Transmission of 10.6 micron radiation by pure water vapor  
at a temperature of 323°K on a course of 2.98 km.

$a$ T%	$b$ $a$ $\Gamma/M^3$	$a$ T%	$b$ $a$ $\Gamma/M^3$	$a$ T%	$b$ $a$ $\Gamma/M^3$
96,I	4,80	78,5	12,I7	55,0	18,90
97,0	4,82	76,7	12,I7	59,4	18,90
92,I	4,83	73,6	14,06	45,6	18,92
90,3	6,89	69,4	14,64	57,5	19,37
89,9	6,89	68,3	15,45	53,8	19,37
86,3	7,86	70,0	15,45	59,2	19,62
84,0	7,96	67,I	16,36	51,5	19,71
88,8	8,05	63,3	16,83	57,5	19,71
83,5	9,75	65,0	16,83	51,7	19,72
83,6	9,75	64,9	17,54	44,0	21,22
83,6	11,33	59,4	17,58	35,I	23,09
78,I	11,43	58,8	18,00	41,0	23,42
75,9	12,08	63,I	18,00	30,9	24,78

Key: (a) transmission, in %; (b) absolute humidity, in  $g/m^3$ .

Table 4

Transmission of 10.6 micron radiation by pure water vapor at a temperature of 353°K on a course of 2.98 km.

a T%	b $\rho$ $r/m^3$	a T%	b $\rho$ $r/m^3$	a T%	b $\rho$ $r/m^3$
99,0	1,84	85,5	10,08	74,6	16,46
97,0	7,04	83,5	13,50	71,0	18,09
93,0	7,06	81,0	13,51	70,0	18,10
86,5	10,06	75,4	16,45		

Key: (a) transmission, in %; (b) absolute humidity, in  $g/m^3$ .

Table 5

Transmission of 10.6 micron radiation by pure water vapor at a temperature of 293°K on a course of 1.99 km.

a T%	b $\rho$ $r/m^3$	a T%	b $\rho$ $r/m^3$	a T%	b $\rho$ $r/m^3$
99,5	0,49	94,8	5,52	71,2	11,16
99,8	1,33	90,2	6,67	79,8	11,23
97,8	1,97	87,3	6,80	76,7	11,55
98,7	2,61	83,0	7,97	69,8	13,08
96,3	3,74	88,9	8,00	63,9	13,90
94,3	3,84	84,4	8,56	62,5	14,20
99,4	4,33	80,8	9,93	60,0	15,12
95,1	4,97	78,7	10,05	55,3	15,40

Key: (a) transmission, in %; (b) absolute humidity, in  $g/m^3$ .

Table 6

Transmission of 10.6 micron radiation by a mixture of water vapor and nitrogen at a temperature of 293°K on a course of 2.98 km.

a	T%	b	$Q$	$r/M^3$	a	T%	b	$Q$	$r/M^3$	a	T%	b	$Q$	$r/M^3$
	92,0		5,90			77,0		9,89			62,0		12,03	
	90,0		5,93			73,0		9,91			61,2		13,41	
	91,0		6,10			70,0		9,98			41,0		14,85	
	82,5		6,90			61,6		11,90						

Key: (a) transmission, in %; (b) absolute humidity, in  $g/m^3$ .

Table 7

Transmission of 10.6 micron radiation by a mixture of water vapor and nitrogen at a temperature of 340°K on a course of 2.98 km.

a	T%	b	$Q$	$r/M^3$	a	T%	b	$Q$	$r/M^3$	a	T%	b	$Q$	$r/M^3$
	86,2		5,20			76,9		10,40			73,0		15,30	
	85,3		7,70			74,2		12,75						

Key: (a) transmission, in %; (b) absolute humidity, in  $g/m^3$ .